Close-coupling calculations of rotational energy transfer in p-H$_2$+HD

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We report quantum-mechanical close-coupling calculations for rotational state resolved cross sections for p-H$_2$+HD collisions. The low temperature limit of p-H$_2$+HD is investigated, which is of significant astrophysical interest in regard to the cooling of primordial gas and the interstellar media. Sharp resonances have been reproduced in the cross sections of some transition states at very low kinetic energies, $E_{kin} \sim 10^{-5}$ eV.

1. Introduction

Energy transfer collisions between H$_2$ and HD molecules, where H is hydrogen and D is deuterium, is of fundamental importance for the astrochemistry of the early Universe and the interstellar medium [1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13]. HD represents the second most abundant primordial molecule after H$_2$ and plays a significant role in the cooling of the primordial gas. The abundance of deuterium is low relative to hydrogen (D/H$\approx 10^{-5}$), however the HD/H$_2$ ratio can be enhanced by an approximate factor of 10^2 due to chemical fractionation [4, 6].

It has been shown, that in the framework of the standard cosmological model the radiation temperature is higher than the matter temperature and molecules become a heating source for the gas. At higher temperatures H$_2$ molecules dominate the heating, however HD molecules dominate the kinetic process at lower temperatures. In addition, the HD molecule is especially important due to its permanent dipole moment and lower rotational constant, which makes the molecule to be an efficient coolant at low temperatures: $T \lesssim 100$K [13]. When H$_2$ molecules are inefficient HD become important in cooling the primordial gas and the interstellar medium. This ability of HD makes these molecules to be very attractive.

Therefore knowledge of the ro-vibrational excitation and de-excitation thermal rate constants in the molecular H$_2$+HD low energy collisions is of fundamental importance in understanding and modeling the energy balance within primordial gas. However, to accurately model the thermal balance and kinetics of such systems one needs accurate state-to-state cross-sections and rate constants $k_{vjv'j'}(T)$.

Experimental measurement of quantum state resolved cross sections and rate coefficients is a very difficult technical problem. On the other hand, accurate theoretical data require precise potential energy surfaces and reliable dynamical treatment of the collision

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processes. The first attempt to construct a realistic full-dimensional ab initio PES for the H_2-H_2 system was done in works [14, 15], and the potential was widely used in a variety of methods and computation techniques. Currently the deuterium chemistry of the eraly Universe has been extensively studied by many researchers. Here we would like to mention works [7, 8] and [3], where the authors carried out quantum-mechanical state-resolved calculations for low and very low temperatures down to 10 K [3], however using of the old and modified H_2-H_2 surface [14].

Nontheless the importance of the H_2+HD in the astrophysical problems makes it vital to carry out new calculations for the system with recently published PES [16]. This is done here in. Moreover, with the current calculations we extend our recent experience for H_2+H_2 at low and very low kinetic energies [17, 18].

As was mentioned above a new extensive study of the hydrogen-hydrogen surface has been recently reported by Boothroyd et al. [16], where the potential energies have been represented at 48180 geometries respectively with a large basis set at the multireference configuration interaction level. In this work we provide the first calculations describing collisions of rotationally excited H_2 and HD molecules using the BMKP PES

$$p\text{-}H_2(j_2) + \text{HD}(j_1) \rightarrow p\text{-}H_2(j_2') + \text{HD}(j_1'). \tag{1}$$

The scattering cross sections are calculated using a non reactive quantum-mechanical close-coupling approach. In the next section we will briefly outline the method and present results for the cross sections for rotational de-excitation of HD in low energy collisions with p-H_2. We compare our results with some previous investigations. Conclusions are presented in Section 3.

2. Method and Results

In this section we provide a brief outline of the quantum-mechanical close-coupling approach used in our calculations. The basis for this methodology was developed in work [19]. The HD and H_2 molecules are treated as linear rigid rotors. For the considered range of kinetic energies of astrophysical interest and for practical astrophysical estimations the rotor model is considered to be adequate for p-H_2+HD collisions [8].

The 4-atomic H_2-HD system is shown in Fig. 1. It can be described by six independent variables: R_1 and R_2 are interatomic distances in each hydrogen molecule, Θ_1 and Θ_2 are polar angles, Φ_2 is torsional angle and R_3 is intermolecule distance. Let us introduce $M_{12} = (m_1 + m_2)(m_3 + m_4)/(m_1 + m_2 + m_3 + m_4)$ and $\mu_{1(2)} = m_{1(3)}m_{2(4)}/(m_{1(3)} + m_{2(4)})$, where the first one is a reduced mass of the pair of two-atomic molecules 12 and 34 and the second ones are reduced masses in hydrogen molecules. As we mentioned, the hydrogen molecules are treated as linear rigid rotors, that is distances $R_1 = 0.7631$ a.u. in H_2 and $R_2 = 0.7668$ a.u. in HD are fixed in this model. We provide a numerical solution for the Schrödinger equation for a $12 + 34$ collision in the center of the mass frame.

The cross sections for rotational excitation and relaxation phenomena can be obtained directly from the S-matrix. In particular, the cross sections for excitation from $j_1 j_2 \rightarrow j_1' j_2'$ summed over the final $m_1' m_2'$ and averaged over the initial $m_1 m_2$ corresponding projections

of the H_2 molecules angular momenta j_1 and j_2 are given by

$$\sigma(j_1', j_2'; j_1 j_2, \epsilon) = \frac{\pi}{(2j_1+1)(2j_2+1)k_{\alpha\alpha'}} \sum_{Jj_{12}j_{12}'LL'} (2J+1)|\delta_{\alpha\alpha'} - S_{\alpha\alpha'}^J(E)|^2. \tag{2}$$

The kinetic energy is $\epsilon = E - B_1 j_1(j_1+1) - B_2 j_2(j_2+1)$. Here E is the total energy in the system, $B_1 = 60.8$ cm^{-1} and $B_2 = 44.7$ cm^{-1} are the rotation constants of the colliding HD and H_2 molecules respectively, J is total angular momenta of the 4-atomic system, $\alpha \equiv (j_1 j_2 j_{12} L)$, where $j_1 + j_2 = j_{12}$ and $j_{12} + L = J$, $k_{\alpha\alpha'} = 2M_{12}(E + E_\alpha - E_{\alpha'})^{1/2}$ is the channel wavenumber and $E_{\alpha(\alpha')}$ are rotational channel energies.

We apply the hybrid modified log-derivative-Airy propagator in the general purpose scattering program MOLSCAT [20] to solve a set of coupled second order differential equations for the unknown radial functions $U_\alpha^{JM}(R)$

$$\left(\frac{d^2}{dR^2} - \frac{L(L+1)}{R^2} + k_\alpha^2\right) U_\alpha^{JM}(R) = 2M_{12} \sum_{\alpha'} \int <\phi_\alpha^{JM}(\hat{r}_1, \hat{r}_2, \vec{R})$$

$$|V(\vec{r}_1, \vec{r}_2, \vec{R})|\phi_{\alpha'}^{JM}(\hat{r}_1, \hat{r}_2, \vec{R}) > U_{\alpha'}^{JM}(R)d\hat{r}_1 d\hat{r}_2 d\hat{R}, \tag{3}$$

We have tested other propagator schemes included in the MOLSCAT code. It was found, that other propagators can also produce quite stable results.

The log-derivative matrix is propagated to large R-intermolecular distances, since all experimentally observable quantum information about the collision is contained in the asymptotic behaviour of functions $U_\alpha^{JM}(R \to \infty)$. The numerical results are matched to the known asymptotic solution to derive the physical scattering S-matrix

$$U_\alpha^J \underset{R\to+\infty}{\sim} \delta_{\alpha\alpha'} e^{-i(k_{\alpha\alpha}R-(l\pi/2))} - \left(\frac{k_{\alpha\alpha}}{k_{\alpha\alpha'}}\right)^{1/2} S_{\alpha\alpha'}^J e^{-i(k_{\alpha\alpha'}R-(l'\pi/2))}, \tag{4}$$

where $k_{\alpha\alpha'} = 2M_{12}(E + E_\alpha - E_{\alpha'})^{1/2}$ is the channel wavenumber, $E_{\alpha(\alpha')}$ are rotational channel energies and E is the total energy in the 1234 system. The method was used for each partial wave until a converged cross section was obtained. It was verified that the results are converged with respect to the number of partial waves as well as the matching radius, R_{max}, for all channels included in our calculations.

The new BMKP PES [16], which is used in these calculations, is a global six-dimensional potential energy surface for two hydrogen molecules. It was especially constructed to represent the whole interaction region of the chemical reaction dynamics of the four-atomic system and to provide an accurate as possible van der Waals well. In the six-dimensional conformation space of the four atomic system the conical intersection forms a complicated three-dimensional hypersurface.

Because the BMKP PES [16] uses cartesian coordinates to compute the distances between four atoms, we needed to devise a fortran program, which converts spherical coordinates used in the close coupling method [20] to the corresponding cartesian coordinates and computes the distances between the four atoms followed by calculations of interatomic interaction forces.

The four atomic system is shown in Fig. 1. Let us introduce the Jacobi coordinates $\{\vec{R}_1, \vec{R}_2, \vec{R}_3\}$ and the radius-vectors of all four atoms in the space-fixed coordinate system

$OXYZ$: $\{\vec{r}_1, \vec{r}_2, \vec{r}_3, \vec{r}_4\}$. We apply the following procedure: $\vec{R}_3$ is directed along OZ axis, the center of mass of the HD molecule is brought into coincidence with the center of $OXYZ$, and the top of the $\vec{R}_3$ is directed to center of mass of H$_2$, as shown in Fig. 1. Now it is apparent, that $\vec{R}_3 = \{R_3, \Theta_3 = 0, \Phi_3 = 0\}$, $\vec{R}_1 = \vec{r}_1 - \vec{r}_2$, $\vec{R}_2 = \vec{r}_4 - \vec{r}_3$, and $\vec{r}_1 = \alpha\vec{R}_1$ and $\vec{r}_2 = (1-\alpha)\vec{R}_1$, where $\alpha = m_2/(m_1 + m_2)$. Next, without the loss of generality, we can adopt the $OXYZ$ system in such a way, that the HD interatomic vector $\vec{R}_1$ lies on the XOZ plane. Then the angle variables of $\vec{R}_1$ and $\vec{R}_2$ are: $\hat{R}_1 = \{\Theta_1, \Phi_1 = \pi\}$ and $\hat{R}_2 = \{\Theta_2, \Phi_2\}$ respectively.

Now one can see, that the cartesian coordinates of the atoms of the HD molecule are: $\vec{r}_1 = \{x_1 = \alpha R_1 \sin\Theta_1, y_1 = 0, z_1 = \alpha R_1 \cos\Theta_1\}$, $\vec{r}_2 = \{x_2 = (1-\alpha)R_1 \sin\Theta_1, y_2 = 0, z_2 = -(1-\alpha)R_1 \cos\Theta_1\}$, and in turn for the H$_2$ molecule we have: $\vec{r}_3 = \{x_3 = -(1-\beta)R_2 \sin\Theta_2 \cos\Phi, y_3 = -(1-\beta)R_2 \sin\Theta_2 \sin\Phi, z_3 = R_3 - (1-\beta)R_2 \cos\Theta_2\}$ and $\vec{r}_4 = \{x_4 = \beta R_2 \sin\Theta_2 \cos\Phi, y_4 = \beta R_2 \sin\Theta_2 \sin\Phi, z_4 = R_3 + \beta R_2 \cos\Theta_2\}$, because $\vec{r}_3 = \vec{R}_3 - (1-\beta)\vec{R}_2$ and $\vec{r}_4 = \vec{R}_3 + \beta\vec{R}_2$, where $\beta = m_4/(m_3 + m_4)$. In such a manner the cartesian and the Jacobi coordinates are represented together for the four-atomic system H$_2$+HD.

Before our production calculations we carried out a large number of test calculations to insure the convergence of the results with respect to all parameters that enter into the propagation of the Schrödinger equation. The same calculations were also done in our previous works [17, 18] for the o-/p-H$_2$+H$_2$ collisions, which involved the intermolecular distance R, the total angular momentum J of the four atomic system, the number of rotational levels to be included in the close coupling expansion N_{lvl}, and others (see the MOLSCAT manual [20]).

We reached convergence for the integral cross sections, $\sigma(j_1', j_2'; j_1 j_2, \epsilon)$, in all considered collisions. For example, for R we used from $R_{min} = 1$ Å to $R_{max} = 22$ Å, we also applied a few different propagators included in the MOLSCAT program. We obtained convergent results in all cases.

Below we present our calculations for the state-resolved cross sections $\sigma(j_1'j_2'; j_1 j_2)(\epsilon)$ in the collision (1). Fig. 2 shows our data for the $(j_1 = 1, j_2 = 0) \rightarrow (j_1' = j_2' = 0)$ and $(j_1 = 2, j_2 = 0) \rightarrow (j_1' = 1, j_2' = 0)$ quantum transitions together with the results of Schaefer's work [3], which applied a modified version of Schwenke's potential [14] and different dynamical quantum-mechanical approach. As can be seen for these transition states the agreement between the two different calculations is excellent. We reproduced sharp resonances in the low velocity region, which are very important in cooling of the astrophysical media. In addition to Fig. 2 we separately show the cross section for only $(j_1 = 1, j_2 = 0) \rightarrow (j_1' = j_2' = 0)$ transition states in Fig. 3. This graph can be directly compared with the corresponding cross section from the Schaefer work [3], please refer to figure 6 of that paper [3]. One can see, that even small peculiarities at around 250 m/s and 450 m/s of the cross section behaviour are reproduced in details.

In the Fig. 4 we present the energy dependence of the cross sections for the $(j_1 = 2, j_2 = 0) \rightarrow (j_1' = j_2' = 0)$ and $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = 0, j_2' = 2)$ quantum-mechanical transition states. For the last transition we obtain very good agreement with the corresponding results of work [3]. However, in the upper graph of Fig. 4 one can see rather large differences in the low velocity region. Our calculations revealed, that the disagreement ranges up to about 100 %.

Finally, significant differences are found in the cross sections from the higher values of the transition states. Fig. 5 presents our results again together with Schaefer's data from [3] for $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = 2, j_2' = 0)$, $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = 1, j_2' = 0)$ and $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = j_2' = 0)$. In this case the disagreement ranges up to one order of magnitude.

Also, as can be seen from the graphs we calculated few new resonances for each of these transitions at a velocity of about 1200 m/s. The biggest value of these resonances is in the cross section $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = 2, j_2' = 0)$. We show this separately in more detail in Fig. 6. The value of the resonance is relatively large and it also might be applicable in important astrophysical processes, such as collisional cooling.

Through this analysis we can now conclude, that the new global BMKP PES can reproduce general behaviour of all considered cross sections in the p-H$_2$+HD collision. For the lower quantum states we obtained sufficient agreement with previous calculations. However, for transition states from higher values, for example, $(j_1 = 2, j_2 = 0)$ the BMKP PES provides rather low cross sections relatively to the corresponding results of work [3].

3. Conclusion

In this letter the state-to-state close-coupling quantum-mechanical calculations for rotational excitation and deexcitation cross sections of the p-H$_2$+HD collision are presented. The linear rigid rotor model for the H$_2$ and HD molecules is applied. The global and newest BMKP surface for the H$_2$-H$_2$ system has been appropriately adopted for the current p-H$_2$+HD collisions. A test of convergence and the results for cross sections with the BMKP PES are obtained for a wide range of kinetic velocities including very low values down to 10 m/s.

Our results revealed, that for low quantum transition states the BMKP surface provides cross sections very close to those obtained in previous works [3, 7], where the authors adopted Schwenke's old H$_2$-H$_2$ PES [14]. However, for some higher quantum states we found significant disagreements with previous results [3] (see Fig. 5). Additionally, in our calculations some new resonances are found in the 1300±100 m/s region for transition states from $j_2 = 2$ and $j_1 = 1$. It was found, that for the specific transition $(j_2 = 2, j_1 = 1) \rightarrow (j_2 = 2, j_1 = 0)$ the value of the resonance is relatively large in the cross section, and it may even stronger influence, for example, the cooling processes in primodial gas and interstellar media. Further detailed calculations for higher quantum transition state cross sections and corresponding thermal rate constants $k_{j_1 j_2 \rightarrow j_1' j_2'}(T)$ for o-/p-H$_2$+HD collisions at low and very low kinetic energies are in progress in our group.

In conclusion, we would like to point out here, that the ultralow energy sector ($T \lesssim$ 1 μK) is of crucial importance now in connection with the recently achieved molecular Bose-Einstein condensates [21, 22, 23, 24, 25, 26]. Therefore, it should also be interesting and useful to apply the current time-independent, quantum-mechanical approach to investigate isotope effects in molecular hydrogen collisions at such ultralow energies. Further, the methodology could be used to carry out new calculations for the important ultralow collisions considered in the works [27, 28, 29], as well as check the conclusions of the recent work [30] involving scattering properties of weakly bound dimers of fermionic atoms.

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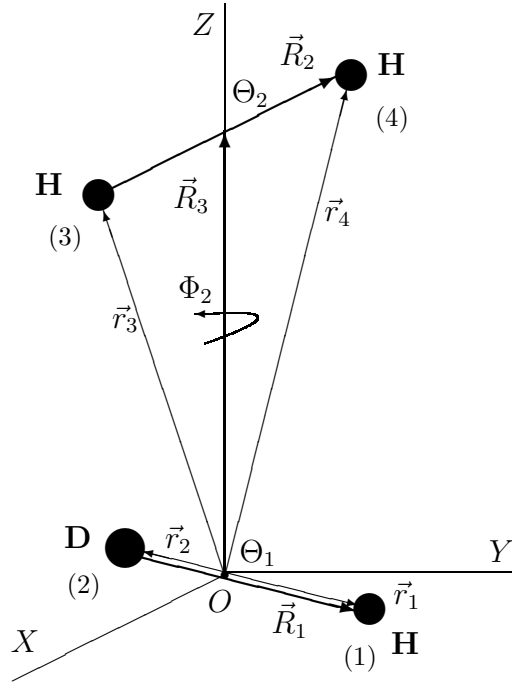30. D. S. Petrov, C. Salomon, and G. V. Shlyapnikov, Phys. Rev. A. 71, 012708 (2005).

Figure 1. Four-atomic coordinates for the p-$H_2(j_2)$+$HD(j_1)$ collision used in this work. $R_1 = 0.7631$ a.u. and $R_2 = 0.7668$ a.u. are fixed interatomic distances in each hydrogen molecule HD and H_2 respectively, Θ_1 and Θ_2 are polar angles of vectors $\vec{R}_1$ and $\vec{R}_2$ respectively, Φ_2 is torsional angle and R_3 is the intermolecular vector, which connects the center of masses of the molecules. Vectors $\vec{r}_1, \vec{r}_2, \vec{r}_3$ and $\vec{r}_4$ represent the cartesian coordinates of the four atoms in the space-fixed $OXYZ$ coordinate system.

Figure 2. Rotational state resolved integral cross sections for p-$H_2(j_2)$ + $HD(j_1)$ $\rightarrow$ $H_2(j_2')$ + $HD(j_1')$. Initial states of HD and H_2 molecules are $j_1 = 1$ and $j_2 = 0$ respectively and corresponding final states are $j_1' = j_2' = 0$. In the bottom plot: $j_1 = 2$, $j_2 = 0$ and $j_1' = 1$, $j_2' = 0$. Calculations are done with the BMKP PES (bold lines), triangles left are corresponding results from work [3].
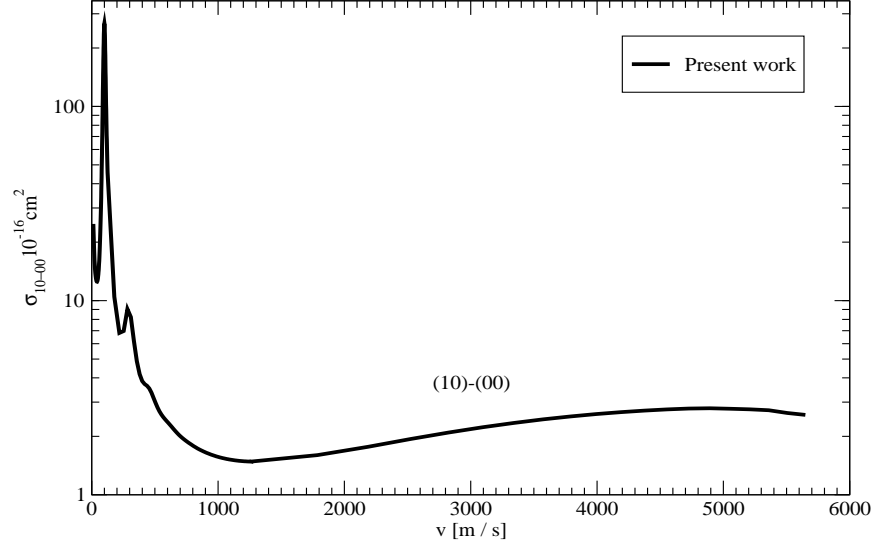

Figure 3. Details of the $(j_1 = 1, j_2 = 0) \rightarrow (j_1' = 0, j_2' = 0)$ rotational transition state cross section in p-$H_2(j_2 = 0)$ + $HD(j_1 = 1)$ $\rightarrow$ $H_2(j_2' = 0)$ + $HD(j_1' = 0)$ to compare with those corresponding cross sections from work [3] figure 6.

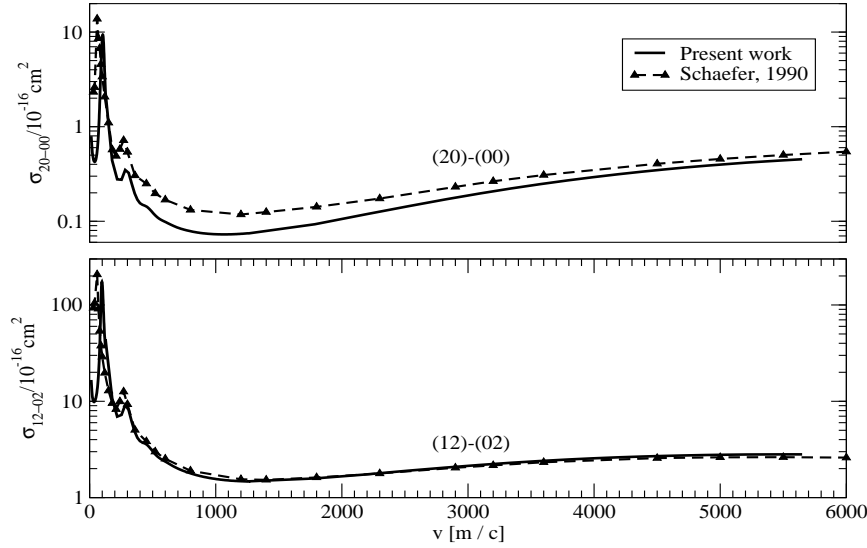Figure 4. Rotational state resolved integral cross sections for p-H$_2(j_2)$+HD$(j_1) \rightarrow$ H$_2(j_2')$+ HD(j_1'). Initial states of HD and H$_2$ molecules are $j_1 = 2$, $j_2 = 0$ respectively and corresponding final states are $j_1' = j_2' = 0$. In the bottom plot: $j_1 = 1$, $j_2 = 2$ and $j_1' = 0$, $j_2' = 2$. Calculations are done with the BMKP PES (bold lines), triangles up are corresponding results from work [3].
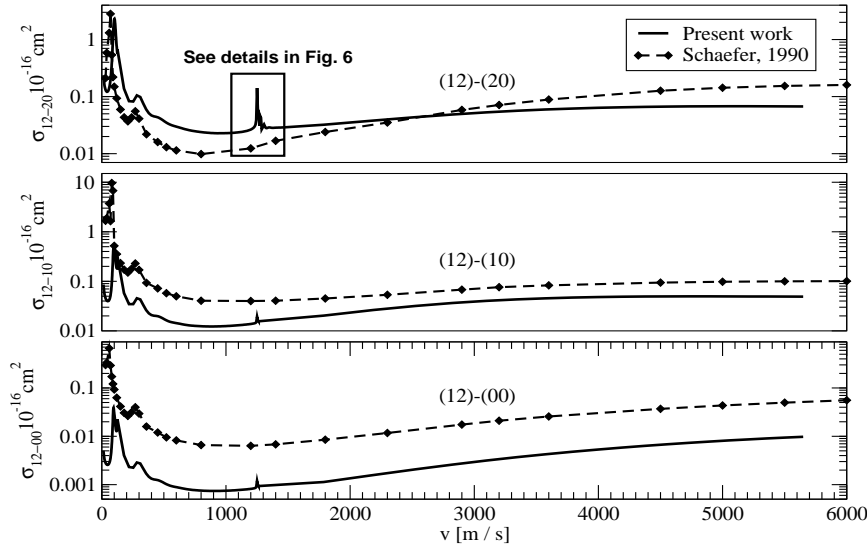

Figure 5. Rotational state resolved integral cross sections for p-H$_2(j_2)$+HD$(j_1) \rightarrow$ H$_2(j_2')$+ HD(j_1'). The initial states of HD and H$_2$ molecules are $j_1 = 1$ and $j_2 = 2$ respectively and corresponding final states are $j_1' = 2, j_2' = 0$ in the upper, $j_1' = 1, j_2' = 0$ in the midle, and $j_1' = j_2' = 0$ in the bottom plots. Calculations are done with the BMKP PES (bold lines), diamonds are corresponding results from work [3].
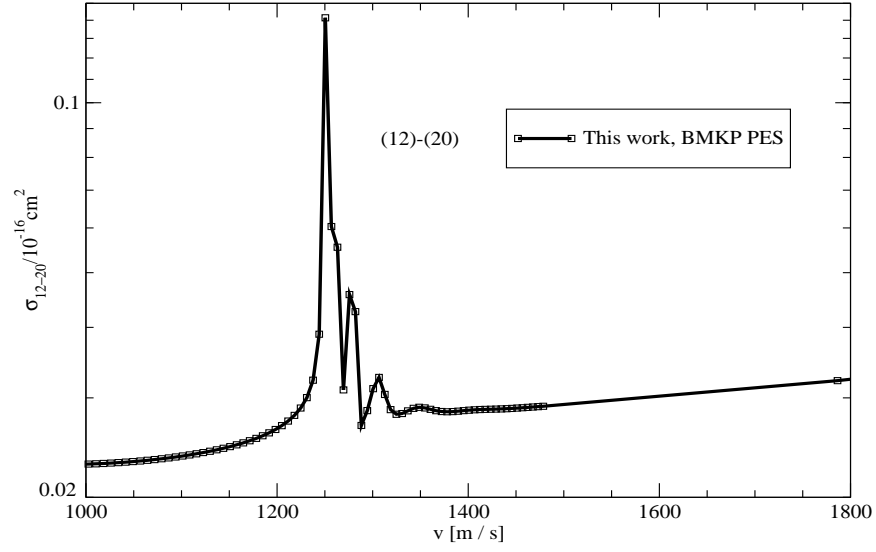
Figure 6. Sharp resonance in the $(j_1 = 1, j_2 = 2) \rightarrow (j_1' = 2, j_2' = 0)$ rotational transition state cros section of p-$H_2(j_2)$ + HD(j_1). The kinetic velocity ranges from 1000 m/s to 1800 m/s in this graph.